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(54) **Silicone and fluorosilicone heat cured filled rubber compositions**

(57) This invention relates to silicone and fluorosilicone rubber compositions incorporating vinyl on end chain functionality and surface modified mineral fillers having reactive moieties in the surface modification such that the mineral filler is cross linked or chemically bound into the polymer matrix of the heat curable rubber composition thereby providing heat curable rubbers possessing improved properties with respect to compression set, swell, and heat age.

The compositions contain a surface-treated potassium aluminosilicate filler. Treatment is chemical modification using a silane, preferably vinyl-tris-(2-methoxyethoxy)silane or an acryloxypropyl-trimethoxy silane. The filler is preferably potassium mica.

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SILICONE AND FLUROSILICONE HEAT CURED FILLED RUBBER COMPOSITIONS

Field of the Invention

This invention relates to silicone and fluorosilicone rubber compositions that incorporate vinyl on end chain functionality and a surface modified mineral filler having reactive moieties in the surface modification such that the mineral filler is cross linked or chemically bound into the polymer matrix of the heat curable rubber composition.

Background of the Invention

Heat cured rubbers are useful in the production of such items as electrical connectors, molded silicone rubber inserts, tubing, hoses, sheeting, gaskets, and the like. Such items are frequently used in applications that expose them to high temperatures, such as might occur in the automotive and aerospace industries. Molded articles prepared from heat cured rubbers suffer from a significant disadvantage in that they tend to suffer from shrinkage when challenged by elevated temperatures. Such shrinkage generally renders the object unsuitable for continued use, particularly in an environment that may experience an elevated temperature. Thus it is desirable to provide a heat cured rubber composition that better resists shrinkage at elevated temperatures.

It is also desirable to provide a heat cured rubber composition that better resists shrinkage at elevated temperatures and that also possesses an enhanced resistance to solvent swell and an improved resiliency.

Heat cured silicone and fluorosilicone rubber compositions are found to possess good processibility and improved resistance to vapor and liquid permeability for various solvents. Such materials thus find applications in automotive gasketing and diaphragms for example. Heat cured silicone or fluorosilicone rubber compositions have an adequate physical property profile. While heat cured silicone rubber compositions possess good elongation and hardness it is desirable to improve other physical properties such as compression set, tensile, and resilience. Improvements in these properties occur partially as a result of the type of reactive groups in the composition of the silicone rubber. Typically these compositions are extended with various fillers to achieve an improvement in the physical property profile of the composite material, processibility, or to lower the cost.

The use of vinyl functional groups within the structure of the heat curable rubber imparts a higher degree of cure, as measured by Monsanto Rheometer, but at the cost of lower elongation. In the case of fluorosilicone rubber compositions a problem of slower cure rates is attributed to the steric bulkiness of the perfluoroalkyl groups in the fluorosilicone compositions. This is overcome or offset by the use of vinyl groups positioned within the framework of the molecule to be distant from the effects of steric overcrowding and thereby increase the state of cure. Only temperature increases will increase the cure rate, however as the number of vinyl groups is increased the state of cure increases.

A recent discovery renders an improvement in the art relating to fluorosilicone heat curable rubber compositions. U. S. patent number 4,960,811 to Evans teaches that incorporation of vinyl groups along the silicone polymer chain as well as the presence of some vinyl groups present on the polymer chain ends that are away from the bulky perfluoroalkyl groups provides a higher state of cure in the cured rubber.

Thermoplastic polymers are finding increasing applications as structural materials. By themselves, thermoplastic polymers may

not exhibit desired physical properties. When used as structural materials, it is a common practice to incorporate a quantity of filler such as a natural or synthetic mineral either as a particulate flake or as a filamentary form to impart rigidity and strength to the thermoplastic polymer. In order to accomplish this end the art recognizes that the particles of the particulate filler must have a high aspect ratio and a high level of rigidity in order to constitute an effective reinforcement. As fillers such as mica are reduced in size, the aspect ratio of the filler material tends to decrease bringing about a loss in the low deformability of the filled composite, a feature imparted by incorporating the filler, see for example United States patent number 4,806,586 to Nakai. Thus the Nakai '586 patent teaches that as the size of the filler is reduced, care must be taken to maintain a high aspect ratio of the filler particles.

The use of filled thermoplastic polymers for structural purposes such as styrene butadiene rubbers and the like has been advanced by the treatment of the filler material with a very thin layer of certain organic compounds. As taught in U. S. patent number 4,425,384 to Brownscombe the organic compounds comprising the surface treating agent are reactive at one end such that they bond in a covalent fashion with the surface of the filler and the other end of the surface treating molecule is such that by the nature of its similarity to the polymer being reinforced the polymer like end of the surface treating moiety interacts with the polymer being reinforced "as if the segment were part of the polymer." As taught in Brownscombe's '384 patent, the surface treating moiety or organic compound must have an "oxygen-reactive" end to chemically bond with the surface of the filler. While Brownscombe's '384 patent teaches the chemical bonding of the surface treating moiety to the surface of a filler material, the other portions of the molecular structure of Brownscombe's surface treating agent are simply polymer-like such that they interact with the polymer being reinforced by the surface treated filler. In Brownscombe's '384 patent while the surface may be chemically modified by the surface

treating agent, the surface treating agent is not capable of chemical reaction or cross-linking with the polymer being reinforced.

When incorporating a filler into a heat curable rubber composition that is flexible as opposed to being rigid or semi-rigid, it has been found that high aspect ratio fillers in rubber compositions generally have a tendency to slice or cut the polymer matrix comprising the rubber when the rubber is flexed or bent because the filler material is typically less flexible than the rubber. Thus, flexing or bending of rubber compositions filled with high aspect ratio fillers tends to mechanically degrade the integrity of the composite. Thus when materials where a high degree of rigidity is desired are to be prepared the use of fillers with high aspect ratios is to be preferred. In contrast, where flexibility is a requirement, low aspect ratio fillers would tend to be preferred. With these guidelines, the range of requirements regarding the aspect ratio of the filler and the end use of the filled polymeric composite may be correlated.

The present invention is based on the discovery that a filler system wherein the filler can be chemically bonded into the polymer matrix constituting the heat cured rubber will produce a heat cured silicone rubber that exhibits superior properties relative to a heat cured silicone rubber containing a comparable filler that is not chemically bonded into the polymer constituting the heat cured rubber. Such improved or superior properties are generally observed to be an increase in tensile, heat age and compression set.

The present invention thus provides a means to produce an improved silicone or fluorosilicone heat curable rubber composition having improved resistance to hydrocarbon oils, compression set, and other physical properties. The present invention further provides a means for preparing articles of manufacture from heat curable rubbers that are improved by being filled with mineral fillers that have been treated with an organofunctional silane.

Summary of the Invention

There is provided in accordance with the present invention a composition for a heat curable silicone rubber comprising a delaminated mineral filler treated with an organofunctional silane and a heat curable silicone or fluorosilicone rubber. The present invention represents an improvement over U. S. Serial No. 07/865546 filed April 9, 1992 and herewith incorporated by reference.

There is also provided in accordance with the present invention a process for preparing a heat curable silicone or fluorosilicone rubber composition comprising said silicone or fluorosilicone and a delaminated mineral filler said filler having been treated with an organofunctional silane.

There is further provided in accordance with the present invention a process for manufacturing articles of manufacture from said heat curable silicone rubber composition comprising a delaminated mineral filler treated with an organofunctional silane.

Detailed Description of the Invention

The present invention is directed to a heat curable silicone or fluorosilicone rubber composition that is curable to form rubber products that have reduced shrinkage at elevated temperatures, increased solvent resistance, and other improved properties. The improved properties of the product result from the use of a novel filler comprising a small particle size mineral filler that has a low aspect ratio, in contrast to the general teachings of the art, said mineral filler being surface treated with a bi- or multi-functional surface treating agent wherein one of the functionalities of the surface treating agent is reactive with the chemical features of the surface of the mineral filler and another functionality of the surface treating agent is reactive with the chemical features of the silicone or fluorosilicone rubber.

The heat curable composition of this invention is composed of two parts, (1) the product obtained by reacting components (A) through (E) at about 25°C to about 180°C; and part (2) a curing catalyst. Preferably a mono- or di- organo substituted peroxide is

the curing catalyst, however others known in the art such as Pt containing catalysts with hydride fluids may also be utilized to effect curing of the compositions of the present invention.

In part (1) of the heat curable composition of this invention, the total sum of (A) and (B) is 100 parts by weight. The amount of (A) is in the range of from 93 to about 98, preferably from about 94 to about 97, and most preferably from about 95 to 96 parts by weight. The amount of (B) corresponds in the complement to (A) such that the sum of (A) and (B) is 100 parts by weight.

The surface treated mineral filler (C) is present in part (1) in an amount within the range of from about 1 to about 40, preferably from about 5 to about 20, and most preferably from about 7 to 15 parts by weight per 100 parts by weight of (A) and (B).

A reinforcing silica filler (D) is present in an amount within the range of from about 5 to about 60, preferably from about 23 to 29, and most preferably from about 23 to 25 parts by weight per 100 parts by weight of (A) and (B).

The amount of condensable polydiorganosiloxane (E) will depend on whether treated or untreated silica filler is utilized in the compositions of the present invention.

Part (1) of the heat curable composition of this invention is prepared by mixing (A) through (E) at a temperature range from about 25°C to about 180°C typically for a period of from about 1 to about 4 hours.

The base polymer (Component (A)) used in the method and composition of this invention is an alkenyl-terminated and silanol-terminated diorganopolysiloxane copolymer comprising units of the formula RR^1SiO and R^2_2SiO , wherein R is an alkyl or fluoroalkyl radical, and R^1 and R^2 are each monovalent hydrocarbon radicals.

In (A), R, R^1 , and R^2 are each either an alkyl or a fluoroalkyl radical containing 3 or more, preferably 3 to 8 carbon atoms, and when the radicals R, R^1 , and R^2 are fluoroalkyl, 1 or more, preferably 1 to 3 fluorine atoms. When the radicals are fluoroalkyl, R is a substituted group such as $-CH_2CH_2R^3$, wherein R^3 is

perfluoroalkyl containing from 1 to 6 carbon atoms, such as perfluoromethyl, perfluoroethyl, up through perfluorohexyl and the like. When the radicals are fluoroalkyl, the R radical is most preferably 3,3,3-trifluoropropyl R¹, and R²

5 When (A) is a fluorosilicone, the RR¹SiO units are present in an amount sufficient to provide a silicon-bonded fluorine content of from about 35 to 37 weight percent. The ratio of alkenyl end groups to silanol end groups is from about 55:45 to about 75:25. The alkenyl on chain content of the copolymer(A) is from about 0%
10 to about 0.06% by weight of (A). The total silicon-bonded alkenyl content of the copolymer is from about 0.05% to about 0.09%. (A) has a viscosity of from about 1,000,000 to about 300,000,000 centipoise at 25° C.

 Component (A) can be prepared by reacting a cyclotrisiloxane
15 containing organo or fluoro-organosubstituent groups, a vinyl terminated sodium silanolate or fluorosilanolate, and a chain stopper that contains a mixture of vinyl terminated silicone or fluorosilicone and silanol terminated silicone or fluorosilicone. The vinyl terminated sodium silanolate or fluorosilanolate used in
20 making (A) is a low molecular weight telomeric fluid containing both sodium silanolate and/or sodium fluorosilanolate and vinyl dimethylsiloxy end groups. This fluid functions as a catalyst for the polymerization of the cyclotrisiloxane to silicone homopolymers and fluids. The vinyl terminated silicone is prepared through the
25 base catalyzed ring opening of silicone cyclic trimer in the presence of appropriate chain modifiers, e.g. divinyltetramethylsiloxane and excess sodium hydroxide. The base is a 4% solution of previously prepared silanolate or fluorosilanolate. The chain modifier used in making (A) can be a mixture containing 100 parts by weight of a
30 vinyl terminated silicone or fluorosilicone polydimethylsiloxane copolymer and from about 2.0 to about 5.0 parts by weight of a silanol terminated silicone or fluorosilicone.

 Component (B) used in the method of this invention functions as a cross linker. It is an alkenyl terminated and silanol terminated

diorganopolysiloxane copolymer, comprising units of the formulae RR^1SiO and R^2_2SiO , wherein R, R^1 , and R^2 are as previously defined herein. The vinyl polymer (B) has a viscosity of from about 1,000,000 to about 300,000,000 centipoise at 25° C. Component (B) can be prepared by reacting a cyclotrisiloxane containing organo and/or fluoro-organo substituent groups, a vinyl terminated sodium silanolate or fluorosilanolate, a methylvinylcyclic trimer, and a vinyl terminated silicone- or fluorosilicone-polydimethylsiloxane copolymer chain stopper.

Component (C) in the composition of this invention is a potassium aluminosilicate filler that has a surface that has been chemically modified by reaction with an organofunctional silane from the group of substituted propyl trimethyl siloxanes where the substitution on the propyl group is terminal and the substituent is selected from one of the following: vinyl-tris-(2-methoxyethoxysilane), 3-methacryloxypropyltrimethoxy silane, and 3-acryloxypropyltrimethoxy silane. The vinyl-tris-(2-methoxyethoxysilane) is preferred.

The alkoxy silane initially reacts with water to hydrolyze the alkoxy groups with the consequence that the resulting silanols are free to interact, react, or hydrogen bond to surface hydroxyl groups on the surface of the potassium aluminosilicate. The preferable organofunctional silanes of primary interest are those that can insert sites of unsaturation. The most preferred of these are the vinyl-containing compounds since they tend to cure at a faster rate in the developing matrix. The level of treatment of the mineral filler with the organofunctional silane ranges from about 0.001 weight per cent to about 3.00 weight percent, more preferably from about 0.001 weight percent to about 1.50 weight percent, and most preferably from about 0.001 weight percent to about 1.00 weight percent.

After treatment with the organofunctional silane the potassium aluminosilicate filler should have a surface area ranging from about 1 to about 20 m²/gm, more preferably from about 2 to about 15 m²/gm, and most preferably from about 3 to about 10

m²/gm. The potassium aluminosilicate filler has an average particle diameter of from about 1.0 to about 20.0, preferably from about 1.0 to about 10.0, and most preferably from about 1.0 to about 5.0 micrometers (microns) and average particle thickness ranging from about 0.5 to about 1.0, preferably from about 0.5 to about 0.8, and most preferably from about 0.45 to about 0.55 micrometers or microns.

The properties of the surface treated potassium aluminosilicate filler are very important to this invention. When the particle size is too great, the particles will tend to break out of the elastomer when it is bent or flexed around a mandrel. Large particle size fillers will not reinforce an elastomer as effectively as smaller particle size fillers since the latter have a higher external surface area.

In a similar fashion the average particle size of the aluminosilicate filler is also critical to this invention. When the average particle size is too large the permeability and swell properties of the final cured product will be greater since the platelets may not fully align and overlap under an applied force.

The actual quantity of filler employed in the composition is also critical because if an insufficient amount of filler is used there will be too great a degree of shrinkage in the final cured product. If too little filler is employed, a reduction in reinforcement and consequently a poorer physical property profile will result. The potassium aluminosilicate (C) has the formula $\text{KAl}_2(\text{AlSi}_3\text{O}_{10})(\text{OH})_2$ or $\text{KAl}_2(\text{AlSi}_3\text{O}_{10})\text{F}_2$. The most preferred potassium aluminosilicate filler for use herein is potassium mica (also known as muscovite), having the formula $\text{KAl}_2(\text{AlSi}_3\text{O}_{10})(\text{OH})_2$, which is a natural hydrous potassium aluminum silicate of the mica group.

The potassium aluminosilicate fillers to be used in the compositions of this invention have a highly delaminated flake structure, i.e. they are micronized. The micronized muscovite mica micas are preferred over the wet ground muscovite micas due to the smaller particle size of the former. The laminar structure of the

micronized mica helps to create a much smaller pore structure in the cured matrix that leads to an improved resistance to compression set, reduced permeation of gases and liquids, and a lower degree of shrinkage of the cured final product.

5 Component (D) in the compositions of this invention is a pre-treated or untreated reinforcing silica filler.

10 The reinforcing silica filler (D) comprises fine powdery silica conventionally known as, for example, fumed silica, precipitated silica, silica aerogel, and the like. The most preferred reinforcing silica for use in the present invention is fumed silica.

15 The term pre-treated as used herein refers to silica fillers that have been treated with a treating agent prior to contacting the silica filler with components (A), (B), (C) and, if present (E). The treating agent reacts with the silanol end groups on the surface of the silica fillers. Alternatively, the silica filler may be untreated (raw) when it is placed in contact with the other components comprising the compositions of this invention. The silica filler is treated prior to the addition of the cure catalyst to the component comprising the compositions of the present invention. The treatment is required, due to the fact that in the absence of the treatment the silanol groups have a tendency to cause structuring of an uncured composition upon standing. When the material is catalyzed, attempts to freshen or re-fresh the batch may result in premature curing and render the batch useless.

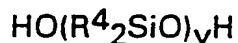
25 The silica filler may be treated prior to contacting the other components comprising the compositions of the present invention. Reference is made to U. S. Patent number 4,529,522 to Evans et al. which is hereby incorporated by reference herein. In the method disclosed in the Evans patent, silica fillers are exposed to the vapor phase diorganosilane direct hydrolyzate at temperatures generally ranging from about 240° C to about 310° C. The direct hydrolyzate are compounds comprising cyclic and linear diorganopolysiloxanes.

30 Preferably the filler is treated in situ according to the method taught in U.S. Patent number 4,724,167 to Evans et al. which is

hereby incorporated by reference herein. According to the '167 Evans patent, silica reinforcing filler is contacted at a temperature of at most 210° C with a liquid condensable diorganopolysiloxane having hydroxy or alkoxy functionality for a time sufficient to
 5 achieve the desired treatment.

The silica filler (D) has a surface area of from about 130 to 325, preferably from about 130 to 225, and most preferably from about 130 to 200 square meters per gram. The surface area of the filler is important because if the surface area is too large, an increase
 10 in the Durometer of the final cured product will result. The increase in the Durometer will be accompanied by an increase in modulus and a decrease in elongation. In contrast, a surface area that is too low will result in a decrease in the Durometer of the final cured product, a decrease in modulus, an increase in elongation and an
 15 increase in tear properties.

Component (E) is a condensable liquid diorganopolysiloxane having the general formula:



wherein R^4 is a monovalent substituted or unsubstituted hydrocarbon radical and y has a value ranging from about 1 to
 20 about 20. Preferably the condensable diorganopolysiloxanes represented by the forgoing formula for (E) are all hydroxy terminated diorganopolysiloxanes. It is also preferred that R^4 be generally 50% or more by number methyl with the balance of the hydrocarbon radicals comprising R^4 be methyl, ethyl, propyl, butyl,
 25 hexyl, and the like; alkenyl such as vinyl or allyl and the like; aryl such as phenyl and the like; cycloalkyl, such as cyclopentyl, cyclohexyl, cycloheptyl, and the like; halogenated alkyl, such as 3-chloropropyl, 4-chlorobutyl, 3,3-difluoroallyl, 3,3,3-trifluoropropyl and the like; halogenated aryl, such as 3-fluorophenyl and the like;
 30 and halogenated cycloalkyl. Where R^4 is halogenated, the preferred R^4 is $-\text{CH}_2\text{CH}_2\text{R}^5$ where R^5 is perfluoroalkyl such as perfluoromethyl, perfluoroethyl, and perfluorohexyl and the like.

The amount of (E) used will depend on whether it is to be

used in situ as a treating agent for the silica filler. If the silica is already treated, it is not required that (E) be present. If (E) is being included in the compositions of the present invention for the purpose of being a plasticizing agent and an anti-structuring agent, then (E) will be present in an amount ranging up to about 4 parts by weight per hundred parts by weight of (A) and (B). If the silica filler is untreated, (E) is used in an amount sufficient to treat the silica filler, which generally ranges from about 5 to about 50 parts by weight of silica.

The curing of the rubber composition of the present invention may be achieved through the use of chemical vulcanizing agents or by high energy radiation. More often, chemical vulcanizing agents are used for the curing operation and any of the conventional curing agents can be used. The preferred curing agents are organic peroxides conventionally used to cure silicone elastomers. Part (2) of the heat curable composition of the present invention is an organic peroxide curing catalyst.

The most suitable peroxide catalysts are compounds of the general formula AOOH, AOOA, or AOOA' wherein A and A' are both an organic radical, especially those compounds wherein one of the oxygens of the peroxide moiety is attached to a tertiary carbon atom in the organic or hydrocarbon radical. Preferred peroxide curing catalysts include, by way of non-limiting examples, t-butylhydroperoxide, cumene hydroperoxide, decaline hydroperoxide, di-t-butylperoxide, dicumyl peroxide, α,α -bis(t-butylperoxy)diisopropylbenzene, t-butyl-cumylperoxide, 2,5-dimethyl-2,5-di(t-butylperoxy)hexyne-3, and 2,5-dimethyl-di(t-butylperoxy)-hexane. More preferred examples are selected from the group consisting of α,α -bis(t-butylperoxy)diisopropylbenzene, t-butyl-cumylperoxide, 2,5-dimethyl-2,5-di(t-butylperoxy)hexyne-3, and 2,5-dimethyl-2,5-di(t-butylperoxy)hexane. The most preferred of these peroxide curing catalysts is 2,5-dimethyl-2,5-di(t-butylperoxy)hexane which is available commercially as a 45 weight per cent mixture with an inert filler under the trade names VAROX®, available from R. T. Vanderbilt

Co., Inc., and LUPERCO® 101XL, available from the Lucidol Division of Pennwalt Corp.

When the curing catalyst used in the preparation of the compositions of the present invention is a peroxide catalyst, the curing catalyst is typically used in an amount sufficiently small to be regarded as catalytic, ranging from about 1.0 to about 2.0, preferably from about 1.0 to about 1.5 and most preferably from about 1.0 to about 1.3 parts by weight per 100 parts by weight (A) and (B) of the heat curable composition.

Examples

The following non-limiting examples are illustrative of the invention.

Example 1

Curable fluorosilicone compositions were prepared via compounding using a dough mixer at a shear rate of 25-30 rpm. 392.0 g of a vinyl terminated high molecular weight fluorosilicone (A) having a vinyl content of 70 - 80 ppm and a Williams plasticity of approximately 200 were mixed with 8.0 g of a vinyl terminated fluorosilicone-methylvinylsiloxo copolymer (B) having a vinyl on chain content of 1.40 wt. % vinyl and a Williams plasticity of approximately 180. 4.0 g of a vinyl terminated polydimethylsiloxane processing aid (C), 2.0 g of a tri-methylsilyl terminated polydimethylsiloxo-methylvinylsiloxo copolymer (D) with a vinyl on chain content of 4.2 wt. %, 0.4 g of 1,3 divinyltetramethyldisilazane (E), and 23.6 g of a disilanol terminated fluorosilicone telomeric fluid (F) containing 6.25 wt. % OH were added and mixed at room temperature for 30 minutes under a nitrogen purge. 92 g of a fumed silica (G) possessing a surface area of approximately 200 m²/g were added incrementally until massed. The nitrogen purge rate was increased by a factor of three and the temperature of the mixture was raised from heat of shear via heating to 170-180° C and held at that temperature for three hours. The mixture was then cooled to below 80° C and 4.0 g of a standard cerium hydroxide stabilizer (H) was added and fully dispersed. The material was discharged from

the dough mixer to yield 524.5 g of a base heat curable rubber composition. This base composition was then mixed with various fillers according to the teachings of the invention and for purposes of comparison. The compositions and the results of the applicable tests are reported in Table 1.

Table 1.

Composition	I	II	III	IV
Component, g				
A	392	392	392	392
B	8	8	8	8
C	4	4	4	4
D	2	2	2	2
E	0.4	0.4	0.4	0.4
F	23.6	23.6	23.6	23.6
G	92	92	92	70
H	4	4	4	4
finely divided mica	32	-	-	-
acrylate surface treated finely divided mica	-	32	-	-
vinyl surface treated finely divided mica	-	-	32	32
Shore A	34	35	36	30
100% Modulus	115	139	159	124
Tensile, psi	1385	1263	1306	1203
Elongation, %	591	529	511	512
Tear B, ppi	146	128	126	99
Specific Gravity, g/cc	1.455	1.462	1.466	1.441
Solvent Swell				
Ref. Fuel C A Wt., %	12.5	12.4	12.3	13.0
70 Hrs./TR A Vol., %	23.2	23.0	22.9	24.2
Compression Set				
22 Hrs/ @ 350° F	14.7	14.7	13.1	13.1
22 Hrs @ 400° F	26.0	25.6	24.4	23.9

Compositions II and III are examples of the invention.

Example 2

Curable compositions were prepared in a manner similar to the procedure followed in example one. 2,784 g of a vinyl terminated fluorosilicone high molecular weight polymer (A) with no vinyl on chain having a Williams plasticity of approximately 200 was
5 mixed with 116 g of the vinyl terminated fluorosilicone-methylvinylsiloxo polymer (B) having a vinyl content of 1.42 wt. % and 43.5 g of a vinyl terminated fluorosilicone-methylvinyl copolymer (D) with a vinyl on chain content of 3.75 wt.%, 29 g of a
10 vinyl terminated polydimethylsiloxane processing aid (C), 4.4 g of 1,3-divinyltetramethyldisilazane (E) and 226.2 g of disilanol terminated fluorosilicone telomeric fluid (F) were added and mixed until dispersed in the gum. 667.0 g of fumed silica (G) was added incrementally until thoroughly massed followed by the addition of
15 580.0 g of surface treated mica according to the precepts of the invention. The same thermal cycle was followed in this example as in example one. After cooling 29.0 g of the standard cerium hydroxide stabilizer (H), 87.0 of standard red iron oxide stabilizer (I), and 20.3 g of a standard magnesium oxide stabilizer (J) were added
20 and thoroughly dispersed. The compound was discharged from the dough mixer to yield 4,357 g. The resulting composition was used to prepare the compositions reported and evaluated in Table 2.

Table 2.

Composition		V	VI
Component, g			
	A	96.0	96.0
5	B	4.0	4.0
	C	1.0	1.0
	D	1.5	1.5
	E	0.15	0.15
	F	7.8	7.8
10	G	23.0	23.0
	H	1.0	1.0
	I	3.0	3.0
	J	0.7	0.7
	acrylate surface treated finely		
15	divided mica	-	20.0
	vinyl surface treated finely		
	divided mica	20.0	-
	Shore A	50	52
	% Modulus	370	382
20	Tensile, psi	1060	1049
	Elongation, %	391	392
	Tear B, ppi	113	109
	Specific Gravity, g/cc	1.530	1.528
	Solvent Swell		
25	M-25 Fuel 70 Hrs @ 60° C		
	Δ Volume %	41.4	41.3
	Compression Set, Method B		
	22 Hrs/ @ 300° F	6.6	12.3
	22 Hrs/ @ 350° F	11.4	18.0
30	22 Hrs @ 400° F	18.7	29.3

Table 2 (continued).

Composition		V	VI
Component, g			
	A	96.0	96.0
5	B	4.0	4.0
	C	1.0	1.0
	D	1.5	1.5
	E	0.15	0.15
	F	7.8	7.8
10	G	23.0	23.0
	H	1.0	1.0
	I	3.0	3.0
	J	0.7	0.7
	acrylate surface treated finely		
15	divided mica	-	20.0
	vinyl surface treated finely		
	divided mica	20.0	-
Cure Parameters			
	Initial Viscosity, in. lbs.	1.42	0.96
20	Viscosity min., in. lbs.	0.56	0.56
	Cure rate, in. lbs./min.	5.90	5.60
	Tg O, min.	3.55	3.45
	State of Cure, in. lbs.	9.28	8.83

Both compositions in Table 2 are examples of the invention. In the
 25 context of the exemplary formulations, the vinyl surface treated
 mica is more preferred.

Example 3.

A curable fluorosilicone composition was prepared using the procedure of examples one and two; however the polymers utilized in the formulation were different from those employed in the previous two examples. 388 g of a vinyl terminated high molecular weight fluorosilicone polymer having 140 - 180 ppm vinyl content and no vinyl on chain and a Williams plasticity of approximately 200, 12 g of a vinyl terminated (140 - 180 ppm vinyl on chain end) fluorosilicone polymethylvinylsiloxo copolymer with 1.42 wt. % vinyl on chain, and 40 g of a vinyl terminated (140 - 180 ppm vinyl on chain end) fluorosilicone polymethylvinylsiloxo high molecular weight copolymer having a vinyl on chain content of 3.74 wt. % were mixed in a dough mixer. 4.0 g of a vinyl terminated polydimethylsiloxane fluid processing aid, 1.2 g 1,3-divinyltetramethyldisilazane, and 48 g of a disilanol terminated fluorosilicone telomeric fluid having approximately 6.2 wt. % hydroxyl functionality were added and kneaded into the gum mixture. 220 g fumed silica having a surface area of approximately 225 m²/g was added incrementally and when fully massed 64 g of either a finely divided mica or a vinyl surface treated mica was added and incorporated into the mass. The thermal processing was the same as in examples one and two. Subsequently standard cerium hydroxide stabilizer and a commercial additive Sartomer 350 ® were added to each composition. The physical properties are summarized in Table 3.

Table 3.

Composition		VII	VIII
Mica component			
5	finely divided mica	present	absent
	vinyl surface treated mica	absent	present
Shore		74.0	76.0
100% Modulus		624	695
Tensile, psi		1096	1005
Elongation, %		236	212
10	Tear B, ppi	115	115
Specific Gravity, g/cc		1.540	1.540

Example 4.

As in the previous examples a base heat curable rubber composition was prepared from fillers and treated fillers. The base composition utilized for purposes of this example consisted of 70 parts by weight of a vinyl chain stopped organopolysiloxane substantially free of vinyl on chain, having a viscosity of from about 3,000,000 to about 100,000,000 centipoise at 25° C, 20 parts by weight of a vinyl on chain organopolysiloxane that is free of vinyl chain stops or terminations and having a vinyl content of from about 5×10^{-3} to about 5 weight percent having a viscosity of from about 3,000,000 to about 100,000,000 centipoise at 25° C, 10 parts by weight of an MDD'Q silicone resin/oil mixture where in the resin M is trimethylsilyl or other tri-organofunctional silane, D is dimethyl and D' is methylvinyl and the resin contains approximately 2.2 weight percent vinyl groups; the oil is an M^{Vi}DM^{Vi} silicone oil having essentially no vinyl on chain, a viscosity of from about 70,000 to about 100,000 centipoise at 25° C, and a vinyl content of approximately 0.06 wt.%, wherein the mixture of oil and resin is about 3 parts oil to two parts resin on a weight for weight basis, 3.0 parts by weight of a silanol terminated or stopped dimethyl fluid having a degree of polymerization of 8, 1.4 parts by weight of a hydride stopped fluid having a hydride content of 0.8 weight percent, 0.12 parts by weight of divinyltetramethyldisilazane, 44 parts by weight of a fumed silica treated with octamethyltetradisiloxane, 3 parts by weight zinc oxide, 1.4 parts by weight of a standard iron octoate treated titanium dioxide stabilizer in a reinforced gum, and 1.5 parts by weight of a standard magnesium oxide stabilizer. To one hundred parts of the base heat curable rubber composition just described, 10 parts of various mineral fillers or extenders were added as described and evaluated in Table 4.

Table 4.

Composition Variables		IX	X	XI	XII	XIII
parts per 100 of heat curable rubber base composition:						
5	finely divided mica	-	10	-	-	-
	vinyl surface treated mica	-	-	10	-	-
	vinyl surface treated mica small particle size	-	-	-	10	-
10	vinyl surface treated clay	-	-	-	-	10
Property Variations:						
Initial:						
	Shore	58	63	63	63	63
	Tensile, psi	1199	1114	1102	1159	1226
15	Elongation, %	573	549	465	520	486
	Tear, ppi	236	267	117	171	245
	100% Modulus, psi	273	332	442	415	362
Heat Aged 70 Hrs @ 400° F:						
	Shore	61	66	65	65	66
20	Tensile, psi	1062	896	965	956	921
	Elongation, %	472	359	348	369	288
	100% Modulus, psi	297	401	474	428	409
% Change Upon Heat Aging:						
	Tensile	-11.4	-19.6	-12.4	-17.5	-24.9
25	Elongation	-17.6	-34.6	-25.2	-29.0	-40.7
Compression Set, %						
	70 Hrs. @ 300° F in					
	5W30 oil (GM FF)*	21.6	13.0	13.3	10.4	16.7
	22 Hrs @ 350° F**	21.8	24.6	20.4	21.7	29.3
30	165 Hrs @ 350° F**	50.8	55.2	55.4	48.7	69.6

* GM FF indicates General Motors Corporation factory fill

** Compression set determined in air

Example 5.

As in the previous examples a base heat curable rubber composition was prepared from fillers and treated fillers. The base composition utilized for purposes of this example consisted of 65 parts of a vinyl terminated or chain stopped organopolysiloxane or mixture thereof that is substantially free of vinyl on chain having a viscosity of from about 3,000,000 to about 100,000,000 centipoise at 25° C; 20 parts by weight of an organopolysiloxane that is substantially free of vinyl having a viscosity of from about 3,000,000 to about 100,000,000 centipoise at 25° C; 15 parts by weight of a vinyl on chain organopolysiloxane that is free of vinyl chain stops or terminations and having a vinyl content of from about 5×10^{-3} to about 5 weight percent having a viscosity of from about 3,000,000 to about 100,000,000 centipoise at 25° C; 3 parts by weight of a silanol terminated or stopped dimethyl fluid having a degree of polymerization of 8 used as a processing aid; 1.2 parts by weight of a hydride stopped fluid cross linking agent having a hydride content of 0.8 weight percent; 0.06 parts by weight of divinyltetramethyldisilazane; 2.6 parts by weight of a standard magnesium oxide stabilizer; 1.3 parts by weight of a standard iron octoate treated titanium dioxide stabilizer in a reinforced gum; 36 parts by weight of a fumed silica, 0.57 parts by weight of a mixture containing 33 wt.% 2,5-dimethyl-2,5-di(t-butylperoxy)hexane, 33 wt.% calcium carbonate, and 33 wt.% of a dimethylsiloxane oil having a viscosity of approximately 30,000 centistokes; and 0.72 parts by weight of a low viscosity silanol or methoxy stopped or terminated low molecular weight siloxane fluid having a viscosity ranging from about 3 to 500 centipoise at 25° C; 20 parts by weight comprising various mineral fillers or extenders were added as described and evaluated in Table 5.

Table 5.

Composition Variables		XIV	XV	XVI	XVII	XVIII
parts per 100 of heat curable rubber base						
5	composition:					
	surface treated mica sm-v	10	-	-	-	-
	finely divided mica	10	10	-	-	20
	surface treated mica sm-p	-	10	10	-	-
	surface treated mica					
10	small particle size	-	-	10	10	-
Property Variations:						
Initial:						
	Shore	56	58	54	56	54
	Tensile, psi	984	1000	1196	1055	1111
15	Elongation, %	640	627	724	697	770
	Tear, ppi	147	141	146	144	205
	100% Modulus, psi	320	387	333	322	244
Heat Aged 70 Hrs @ 400° F:						
	Shore	57	60	56	57	57
20	Tensile, psi	887	798	931	850	809
	Elongation, %	553	408	559	542	585
% Change Upon Heat Aging:						
	Tensile	-9.9	-20.2	-22.2	-19.4	-27.2
	Elongation	-13.6	-34.9	-22.8	-22.2	-24.0
25	Compression Set, %					
	22 Hrs @ 350° F	27.7	30.9	24.2	26.2	33.6

The stabilizers utilized in the examples were laboratory equivalents of commercially utilized stabilizing agents:

30 Cerium hydroxide stabilizer - finely divided cerium hydroxide powder such that 99% passes through a 250 mesh screen dispersed in an M-stopped polydimethylsiloxane (PDMS) fluid having a viscosity of 30,000 cps. The weight ratio of cerium (IV) hydroxide to PDMS fluid is 3:1 respectively.

Magnesium hydroxide stabilizer-siloxane gum that has 0.2 wt.% vinyl on chain. The ratio of weights is 1:3 magnesium oxide to PDMS gum.

5 Iron octoate treated titanium dioxide - 52 parts by weight of a silicone gum, 10 parts by weight methylcyclotetrasiloxane treated fumed silica, 5 parts by weight of 6% iron octoate, and 33 parts by weight of fumed titanium dioxide. The material is kneaded in a dough mixer under conditions of shear to achieve a dispersion of the components in the gum.

Claims

1. A heat curable silicone rubber composition comprising a polymer system and a surface treated potassium aluminosilicate filler, said heat curable rubber composition comprising:

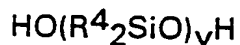
5 (A) an alkenyl-terminated and silanol-terminated diorganopolysiloxane copolymer comprising units of the formula RR^1SiO and R^2_2SiO , wherein R is an alkyl or fluoroalkyl radical, and R^1 and R^2 are each monovalent hydrocarbon radicals, wherein R, R^1 , and R^2 are each either an alkyl or a fluoroalkyl radical containing 3 or more, preferably 3 to 8 carbon atoms, and when the radicals R,
10 R^1 , and R^2 are fluoroalkyl, 1 or more fluorine atoms, wherein when the radicals are fluoroalkyl, R is $-CH_2CH_2R^3$, wherein R^3 is a perfluoroalkyl group containing from 1 to 6 carbon atoms said copolymer having a viscosity of from about 1,000,000 to about 300,000,000 centipoise at 25° C;

15 (B) an alkenyl terminated and silanol terminated diorganopolysiloxane copolymer, comprising units of the formulae RR^1SiO and R^2_2SiO , wherein R, R^1 , and R^2 are as previously defined and having a viscosity of from about 1,000,000 to about 300,000,000 centipoise at 25° C;

20 (C) a potassium aluminosilicate filler in an amount up to about 40 parts per hundred based on the sum of components (A) and (B) wherein said potassium aluminosilicate filler has been chemically modified by reaction with an organofunctional silane selected from the group consisting of substituted propyl trimethyl siloxanes where
25 the substitution on the propyl group is terminal and the substituent is selected from the group consisting of vinyl-tris-(2-methoxyethoxysilane), 3-methacryloxypropyltrimethoxy silane, and 3-acryloxypropyltrimethoxy silane;

30 (D) a silica filler in an amount up to about 50 parts based on the sum of components (A) and (B) selected from the group consisting of fumed silica, precipitated silica, and silica aerogel;

(E) a condensable liquid diorganopolysiloxane having the general formula:



in an amount up to about 4 per hundred based on the sum of components (A) and (B) wherein R^4 of said condensable liquid diorganopolysiloxane is a monovalent substituted or unsubstituted hydrocarbon radical and y has a value ranging from about 1 to about 20; and

2. The heat curable rubber composition of claim 1 wherein the amount of component (A) ranges from about 93 to about 98 parts by weight and the amount of component (B) is determined such that the sum by weight of components (A) and (B) is 100 parts by weight.
3. The heat curable rubber composition of claim 1 or claim 2 wherein the amount of component (A) ranges from about 94 to about 97 parts by weight and the amount of component (B) is determined such that the sum by weight of components (A) and (B) is 100 parts by weight.
4. The heat curable rubber composition of any preceding claim wherein the amount of component (A) ranges from about 95 to about 96 parts by weight and the amount of component (B) is determined such that the sum by weight of components (A) and (B) is 100 parts by weight.
5. The heat curable rubber composition of any preceding claim wherein component (C) is present in an amount between 10 and 40 parts by weight per hundred parts by weight of the sum of components (A) and (B).
6. The heat curable rubber composition of any preceding claim wherein component (C) is present in an amount between 5 and 20 parts by weight per hundred parts by weight of the sum of components (A) and (B).
7. The heat curable rubber composition of any preceding claim wherein component (C) is present in an amount between 7 and 15 parts by weight per hundred parts by weight of the sum of components (A) and (B).
8. The heat curable rubber composition of any one of claims 1 to 7 wherein the potassium aluminosilicate filler, component (C), has been treated with an organofunctional silane selected from the group consisting of substituted propyl trimethyl siloxanes where the substitution on the propyl group is terminal and the substituent is selected from the group consisting of vinyl-tris-(2-methoxyethoxysilane), 3-methacryloxypropyltrimethoxy silane, and 3-acryloxypropyl-trimethoxy silane wherein said treatment ranges in an amount of from about 0.001 weight percent to about 3.00 weight percent.

9. The heat curable rubber composition of any one of claims 1 to 7 wherein the potassium aluminosilicate filler, component (C), has been treated with vinyl-tris-(2-methoxyethoxysilane) wherein said treatment ranges in an amount of from about 0.001 weight percent to about 3.00 weight percent.

10. The heat curable rubber composition of any preceding claim wherein component (C) has a surface area ranging from about 1 to about 20 m²/g.

11. The heat curable rubber composition of any preceding claim wherein component (C) has an average particle diameter of from about 1.0 to about 20.0 micrometers and an average particle thickness ranging from about 0.5 to about 1.0 micrometers.

12. A heat cured rubber composition comprising the heat curable rubber composition of any preceding claim.

13. A gasket manufactured from the heat curable rubber composition of any preceding claim.

14. A process for preparing a heat curable rubber composition comprising the steps of:

(a) treating a potassium aluminosilicate filler with an organofunctional silane selected from the group consisting of substituted propyl trimethyl siloxanes where the substitution on the propyl group is terminal and the substituent is selected from the group consisting of vinyl-tris-(2-methoxyethoxysilane), 3-methacryloxypropyltrimethoxy silane, and 3-acryloxypropyltrimethoxy silane; and mixing said treated filler with,

(b) A heat curable silicone rubber composition comprising a polymer system comprising:

(A) an alkenyl-terminated and silanol-terminated diorganopolysiloxane copolymer, in an amount of up to about 100 parts by weight, comprising units of the formula RR^1SiO and R^2_2SiO , wherein R is an alkyl or fluoroalkyl radical, and R^1 and R^2 are each monovalent hydrocarbon radicals, wherein R, R^1 , and R^2 are each either an alkyl or a fluoroalkyl radical containing 3 or more, preferably 3 to 8 carbon atoms, and when the radicals R, R^1 , and R^2 are fluoroalkyl, 1 or more fluorine atoms, wherein when the radicals are fluoroalkyl, R is $-CH_2CH_2R^3$, wherein R^3 is a perfluoroalkyl group containing from 1 to 6 carbon atoms said copolymer having a viscosity of from about 1,000,000 to about 300,000,000 centipoise at

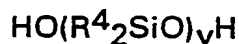
25° C;

(B) an alkenyl terminated and silanol terminated diorganopolysiloxane copolymer, in an amount of up to about 100 parts by weight, comprising units of the formulae RR^1SiO and R^2_2SiO , wherein R, R^1 , and R^2 are as previously defined and having a viscosity of from about 1,000,000 to about 300,000,000 centipoise at 25° C; and

(c) adding said treated potassium aluminosilicate filler, (C) in an amount up to about 40 parts per hundred based on the sum of components (A) and (B) wherein said potassium aluminosilicate filler has been chemically modified by reaction with an organofunctional silane selected from the group consisting of substituted propyl trimethyl siloxanes where the substitution on the propyl group is terminal and the substituent is selected from the group consisting of vinyl-tris-(2-methoxyethoxysilane), 3-methacryloxypropyltrimethoxy silane, and 3-acryloxypropyltrimethoxy silane; and

(d) adding a silica filler (D) in an amount up to about 50 parts based on the sum of components (A) and (B) selected from the group consisting of fumed silica, precipitated silica, and silica aerogel; and

(e) adding a condensable liquid diorganopolysiloxane (E) having the general formula:



in an amount up to about 4 per hundred based on the sum of components (A) and (B) wherein R^4 of said condensable liquid diorganopolysiloxane is a monovalent substituted or unsubstituted hydrocarbon radical and y has a value ranging from about 1 to about 20; and

(f) adding an organic peroxide curing agent (F) in an amount of from 0.01 to up to about 5 parts per hundred based on the sum of components (A) and (B).

Examiner's report to the Comptroller under Section 17
(The Search report)

Relevant Technical Fields

Search Examiner
DIANE DAVIES

- (i) UK Cl (Ed.N) C3T: TBA, TBX
(ii) Int Cl (Ed.6) C08L 83/04

Date of completion of Search
7 FEBRUARY 1995

Databases (see below)

(i) UK Patent Office collections of GB, EP, WO and US patent specifications.

Documents considered relevant following a search in respect of Claims :-
1 TO 14

(ii) ONLINE DATABASES: CAS-ONLINE, EDOC, WPI, JAPIO

Categories of documents

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- A:** Document indicating technological background and/or state of the art. **&:** Member of the same patent family; corresponding document.

Category	Identity of document and relevant passages		Relevant to claim(s)
A	EP 0567253 A	(GENERAL ELECTRIC CO) whole document: heat-curable silicone rubber compositions containing potassium aluminosilicate as filler	
A	EP 0520777 A	(GENERAL ELECTRIC CO) whole document: heat-curable fluorosilicone rubber compositions containing potassium aluminosilicate as filler	

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